Hip Implant Corrosion Mechanisms and Effects:

Mechanically Assisted Corrosion, Crevices and Voltage Effects

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Potential Conflicts

- Consultant to and/or research contracts with
  - Medtronic
  - Stryker Orthopedics
  - Depuy Orthopedics
  - Biomet, Inc.
- Other Potential Conflicts
  - Editor-in-Chief, Journal of Biomedical Materials Research – Part B: Applied Biomaterials
  - Past President, Society for Biomaterials

Mechanically Assisted Corrosion

- Tribocorrosion (wear and corrosion)
- Fretting Corrosion (fretting and corrosion often in presence of a crevice)
  - Fretting = small scale cyclic motion (< 100 um) between two opposing surfaces
- Stress Corrosion Cracking
- Stress Enhanced Corrosion
- Each is present in hip replacements where metals are stressed, abraded, worn or fretted
- Crevice-like environments add to the severity and complexity of the corrosion
- Fretting INITIATED Crevice Corrosion – Fretting can produce the conditions for run-away corrosion (where fretting (or wear) is no longer required)
  - Fretting = Match
  - Crevice Corrosion = Fire

Some Basic Facts of Importance

- You **CANNOT HAVE WEAR** of Metal Alloy Hip Implants **WITHOUT CORROSION!**
  - (But, you can have corrosion without wear)

- WEAR and CORROSION ARE COUPLED and NON-LINEAR
  - Wear -> Oxide Film Abrasion -> Corrosion -> Voltage Drop ->
    -> Altered Oxide -> Altered Wear

- Oxide Films on Alloy Surfaces are Critical to Mechanically Assisted Corrosion Behavior and Corrosion Resistance

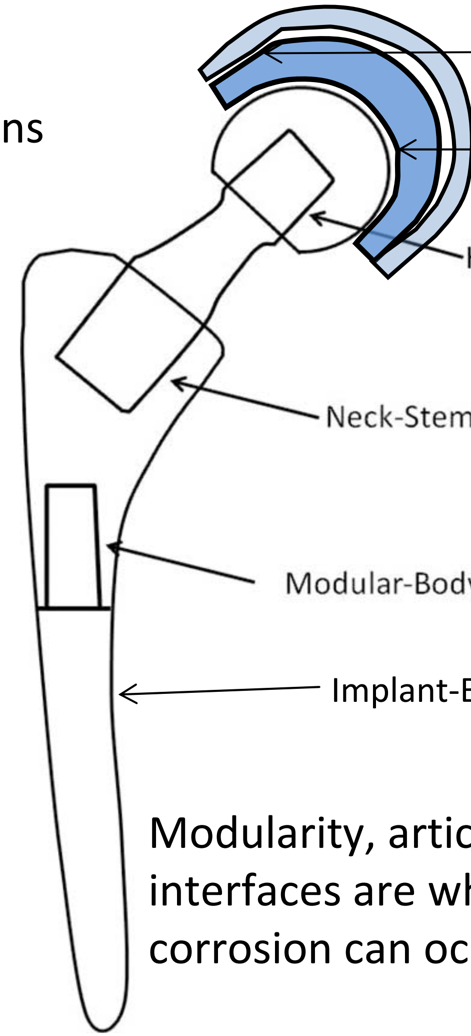
- With Corrosion: Voltage drops (cathodic excursions) and currents are generated which can affect the implant
  - depends on area abraded,
  - crevice geometries
  - and area available for reduction reactions

- Cathodic excursions have significant effects on the local biological reaction. **It's not just about the metal ions and debris!**

Hip Prosthesis Corrosion Sources

Examples of Current Modular Designs

Not indicative of anything corrosion related



Modularity, articulating surfaces and other interfaces are where mechanically assisted corrosion can occur.

Most severe corrosion observed at modular tapers
Corrosion at one location affects all others (e.g., voltage drops)

In-Vivo Corrosion of Modular Tapers: Head-Neck Tapers: 1993

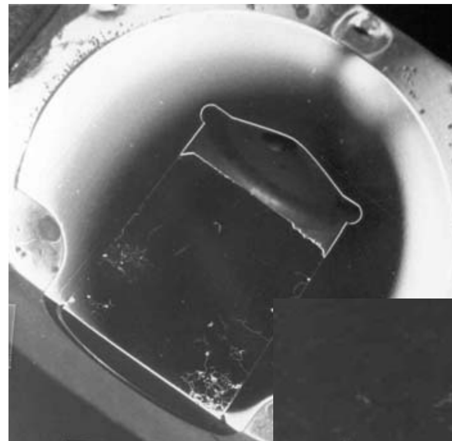
Gilbert, et al., JBJS 1993

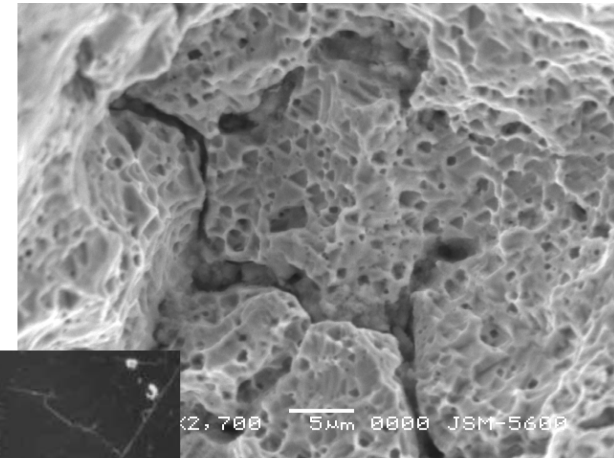
Co-Cr-Mo/Co-Cr-Mo

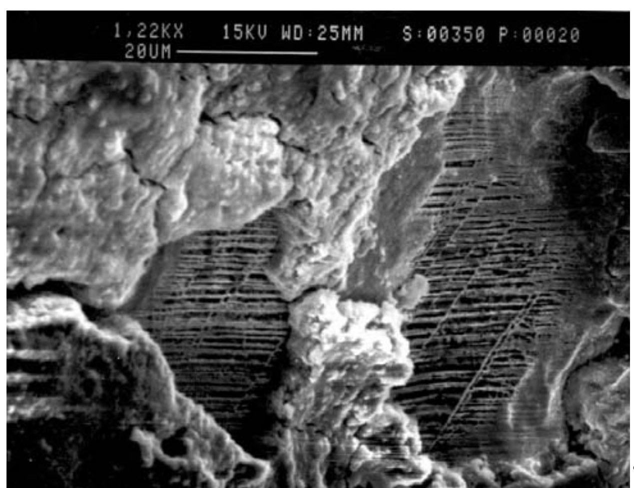
We have known since the late 1980’s about modular implant corrosion (Svensson et al, 1988, JBJS(A), Fulminant pseudotumor with Co-Cr/CoCr modular taper)

All currently-used alloy combinations are known to be susceptible to attack (Ti, CoCrMo, 316L SS)

Passive oxide films on the surface are central to mechanism of attack.







Gilbert et al, JBMR-A, 1993

Ti-6Al-4V/Co-Cr-Mo

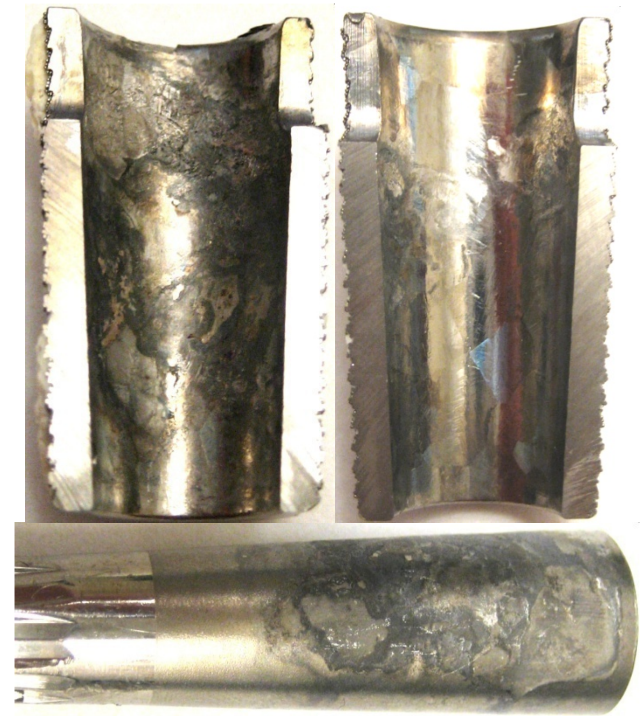
Modular Body Interfaces: Ti6Al4V / Ti6Al4V Interfaces: 2009

Company A

- Infection-related
- 22 months

Company B

- Infection-related
- Unknown -1?



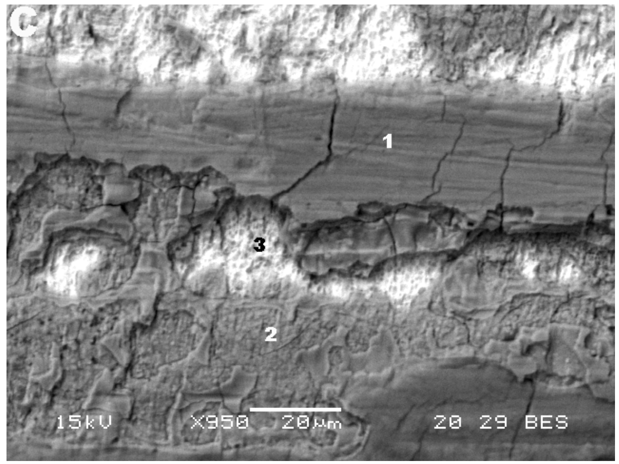
Company C

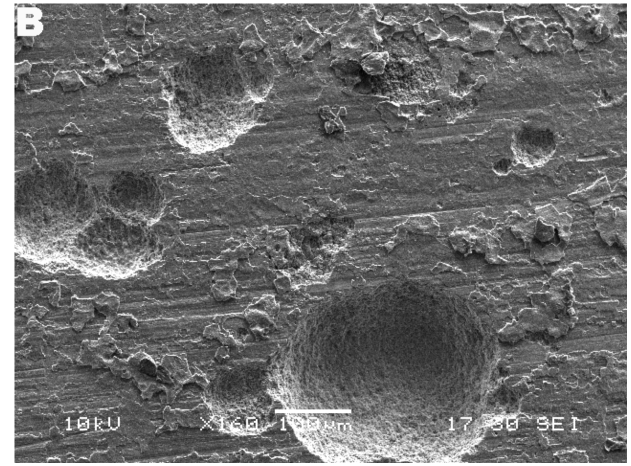
- Pain
- 27 months

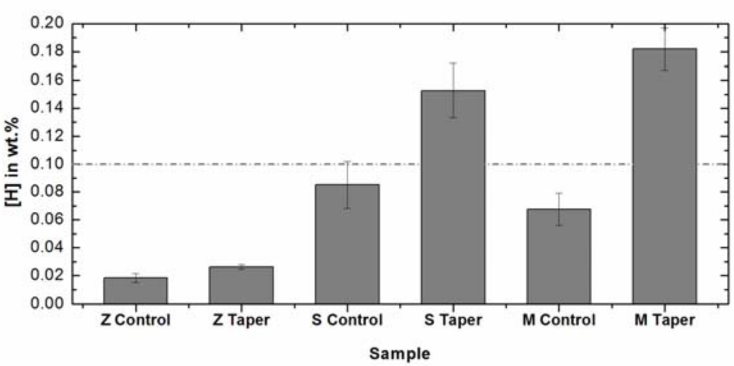
Rodrigues, et al., JBMR-B, 2009

Ti/Ti Modular Tapers:

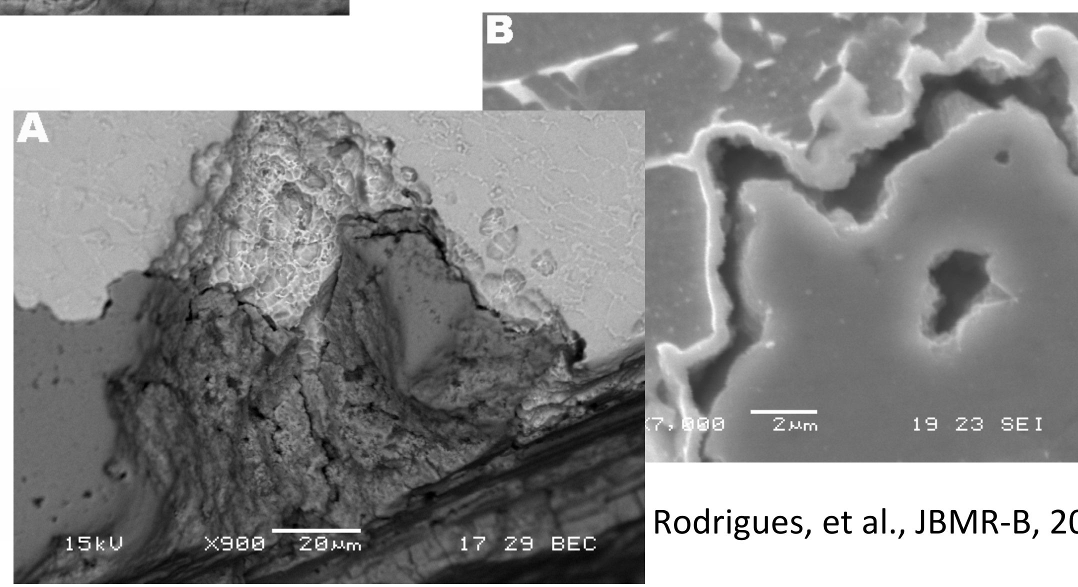
Fretting Crevice Corrosion is STILL a problem







Pitting Corrosion and Hydrogen Embrittlement have been observed,



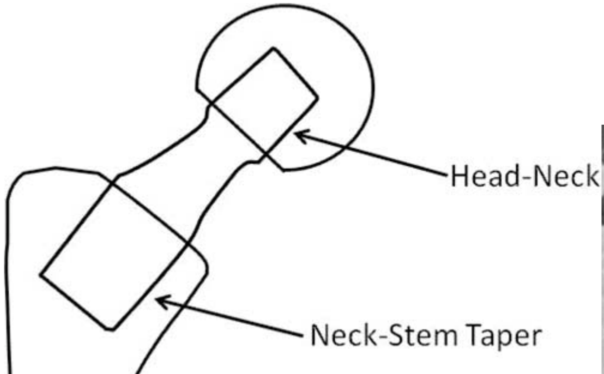
Rodrigues, et al., JBMR-B, 2009

Fretting INITIATED Crevice Corrosion

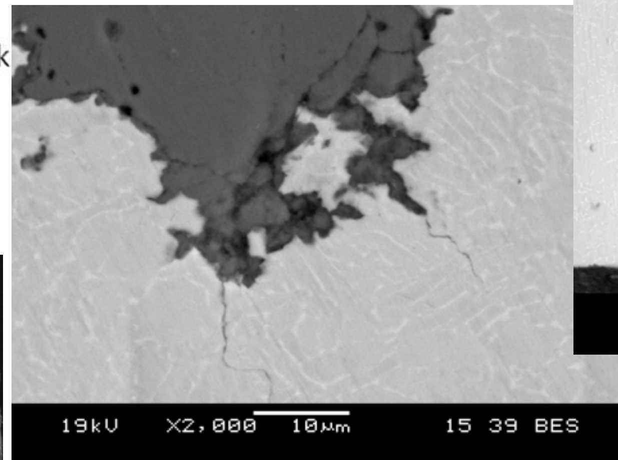
Modular Neck Corrosion: 2012

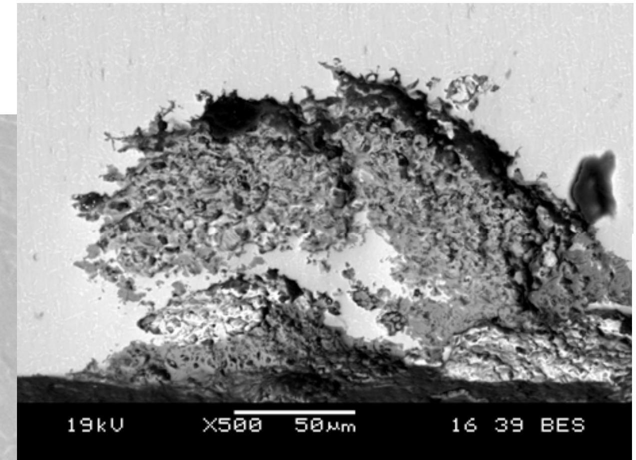
In-Vivo Oxide-Induced Stress Corrosion Cracking in Ti-6Al-4V Modular Neck-stem Tapers

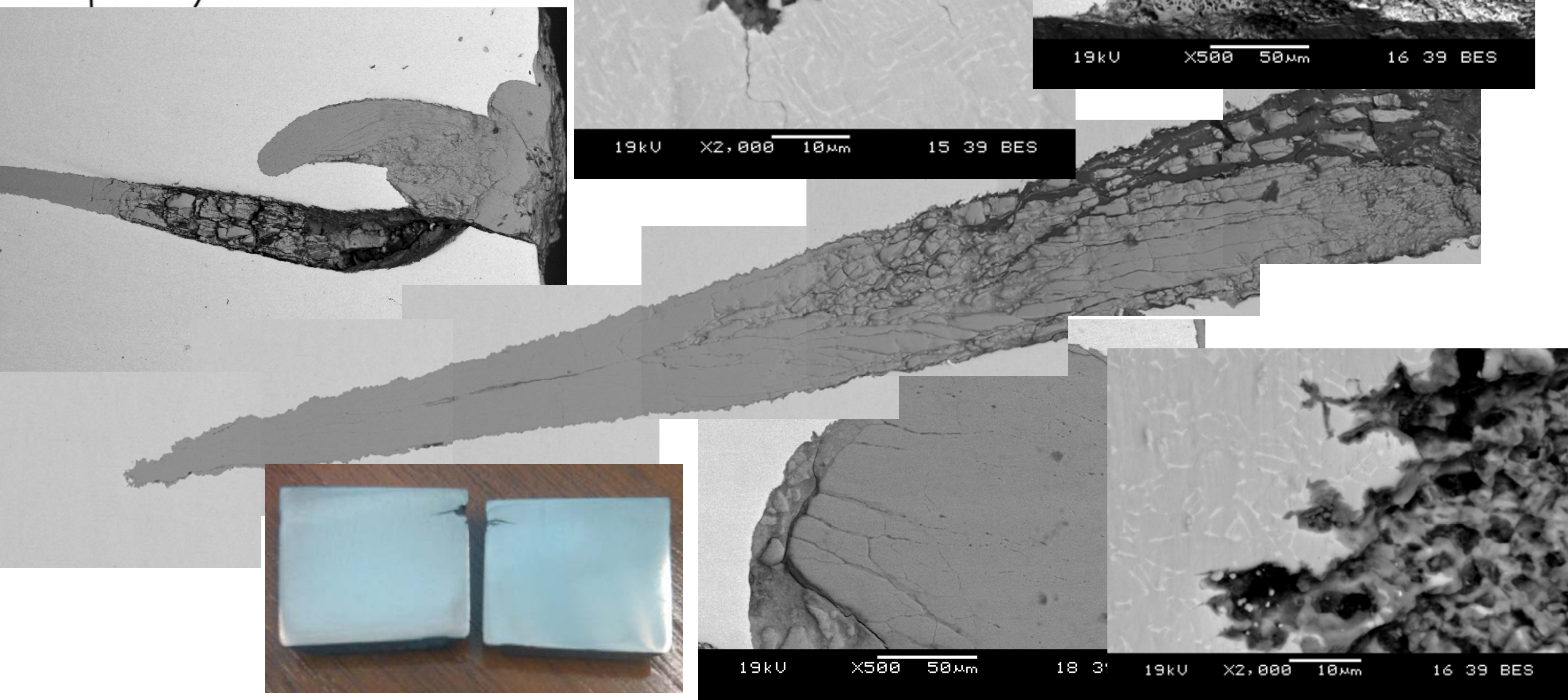
Medial proximal neck-stem taper cracking



Gilbert et al., 2012, JBMR-B

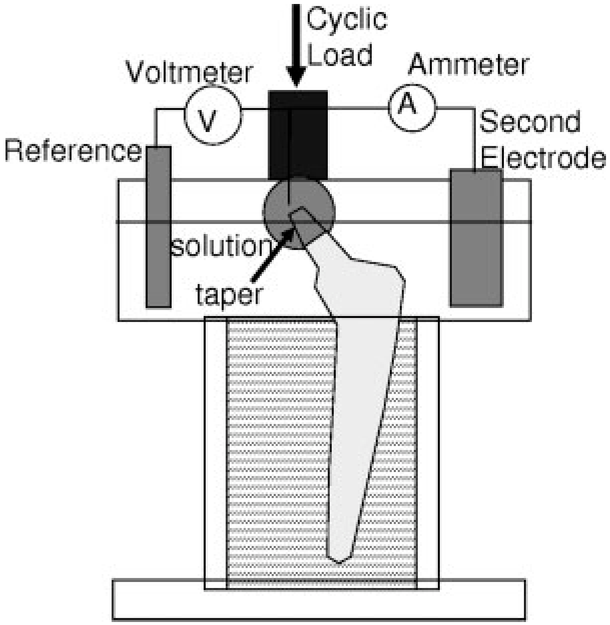


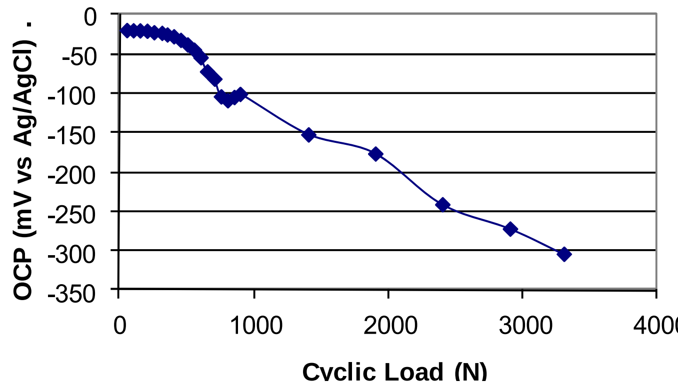


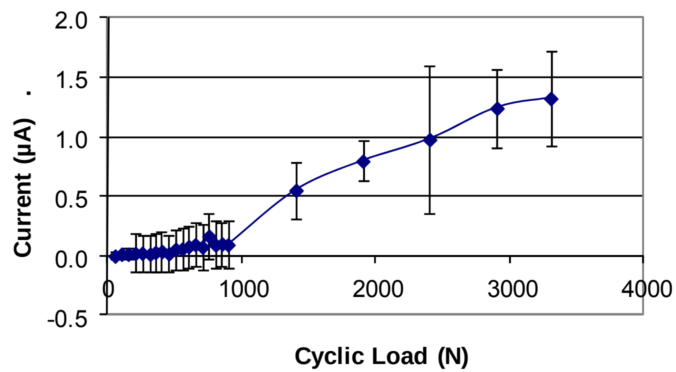


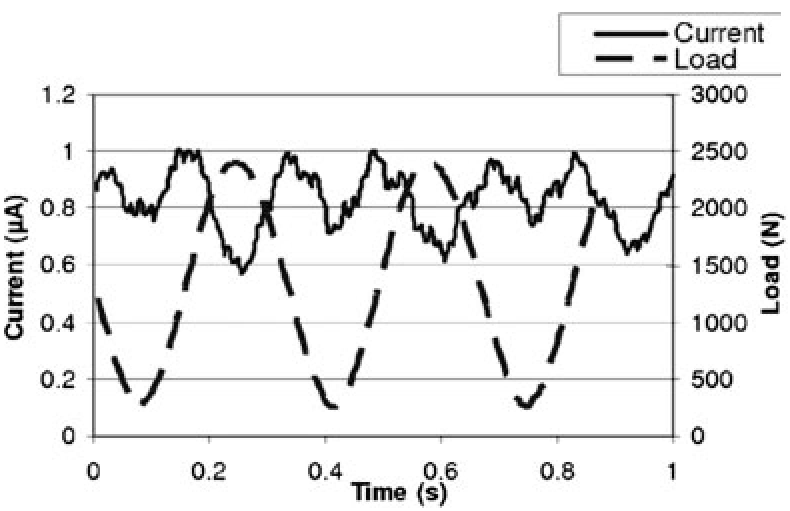
In-Vitro Fretting Corrosion Testing

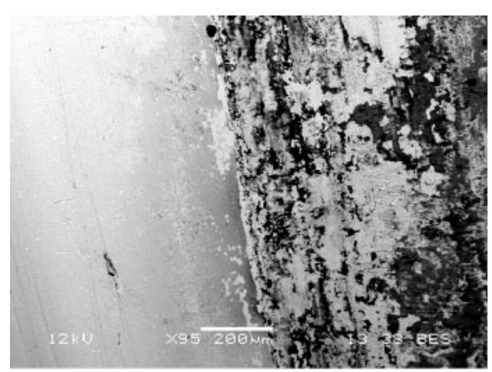
316L SS Stem/CoCrMo Head Couples



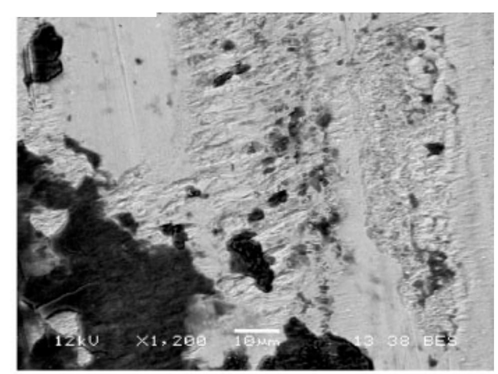








a



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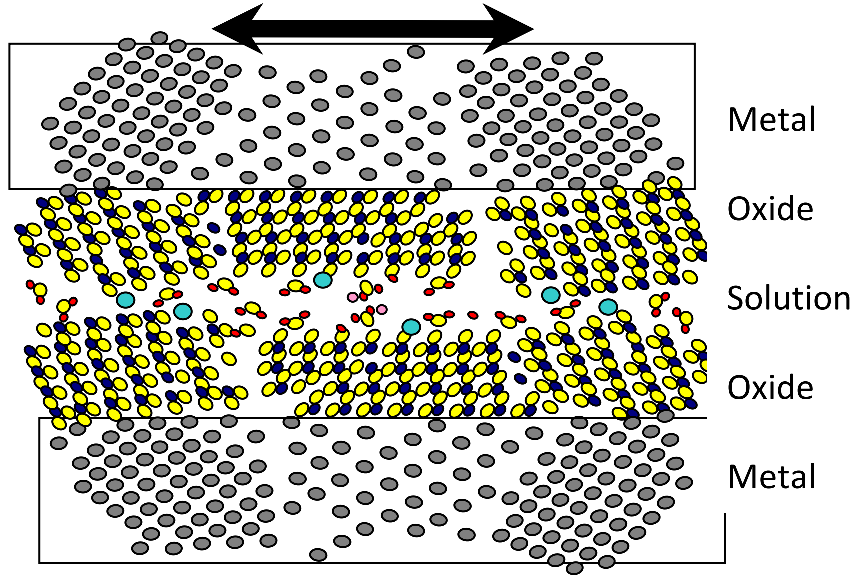
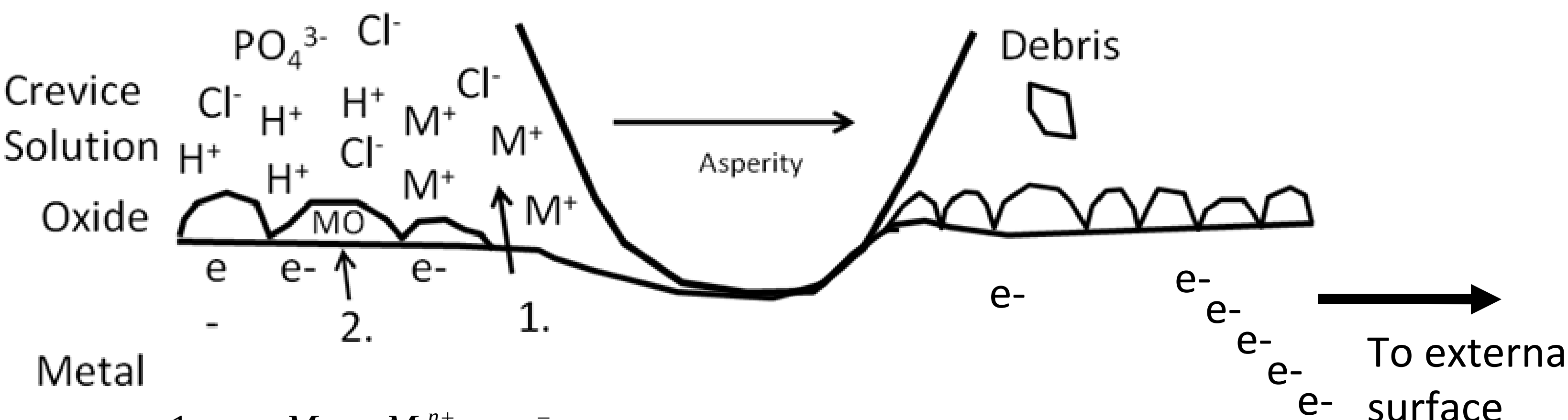
Electrochemistry of Fretting Interfaces

Metal ions, phosphate, chloride, hydrogen ions accumulate in crevice

Fretting currents consist of dissolution and repassivation reactions

Oxidation debris accumulates in crevice





1. $M \rightarrow M^{n+} + ne^-$
2. $M + H_2O \rightarrow MO + 2H^+ + 2e^-$

Excess electrons decrease voltage of implant

Crevices and Spatially Separated Half-Cell Reactions

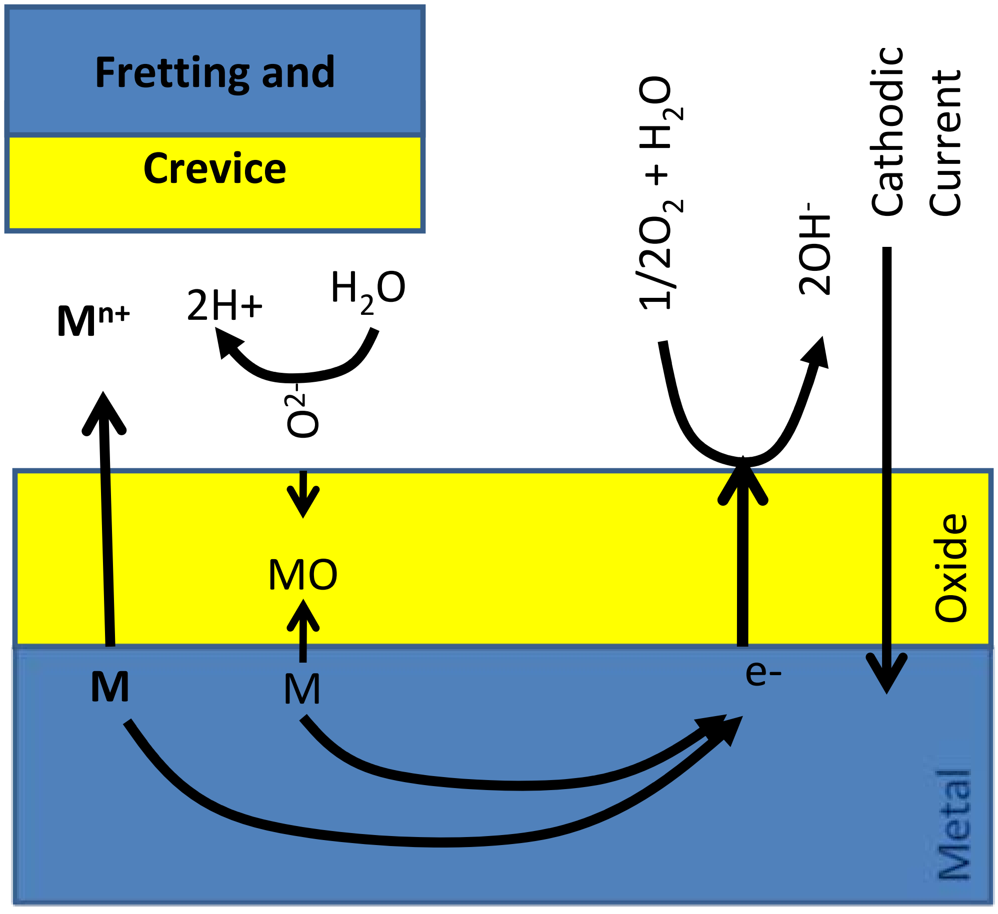
- Crevice and fretting localize oxidation
  - Oxide film repassivation
  - Metal ion dissolution

- Outside Crevice
  - Reduction (multiple, biologically based species available)

- Note: in crevice
  - Oxygen depletion
  - pH drops
  - Cl^- , PO_4^{3-} increases to balance M^+

- Note: Fretting disrupts oxide in crevice and accelerates oxidation by 6 orders of magnitude.

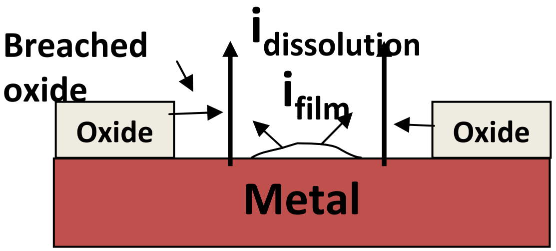
- Build up of electrons drops voltage of surface



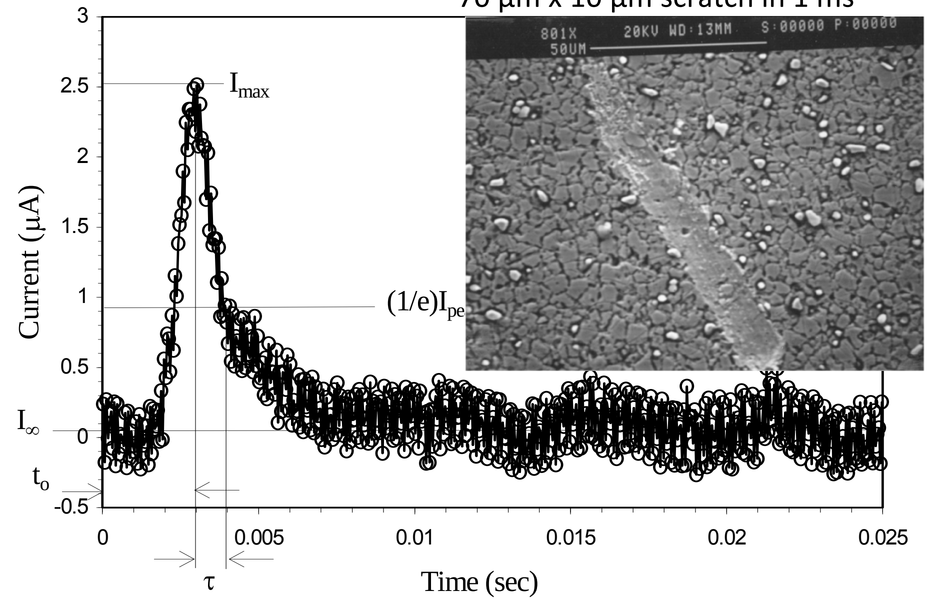
Oxide Abrasion: High Speed Scratch Testing Ti- and CoCr Alloy

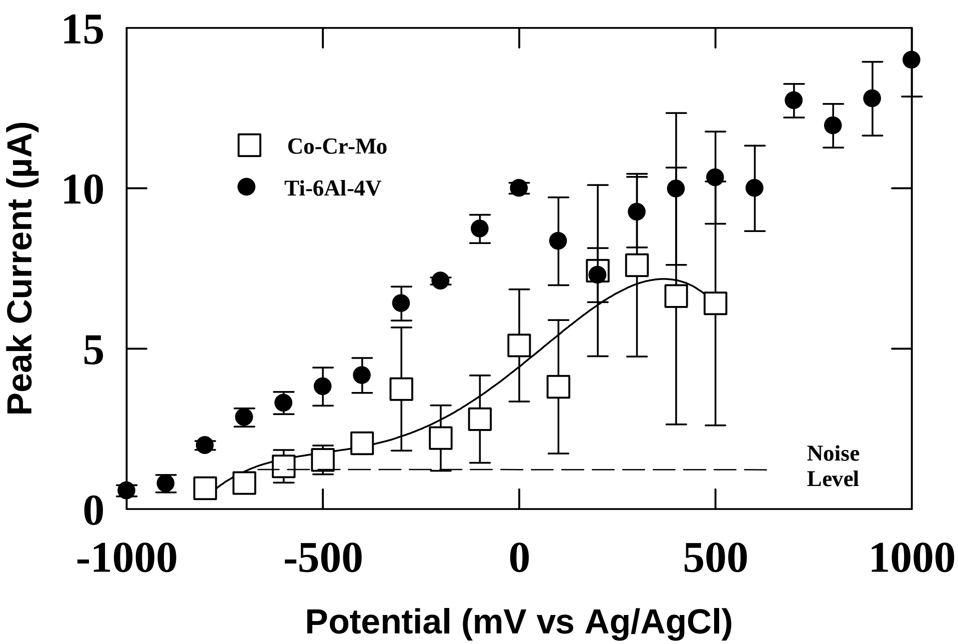
- 2.5 µA for 700 µm² results in 0.35 A/cm² current density at scratch site
- 10^6 higher current densities than at passive oxides.

Ambrose model of breached oxide



70 µm x 10 µm scratch in 1 ms





$$M \rightarrow M^{n+} + ne^-$$

$$mM + nH_2O \rightarrow M_mO_n + 2nH^+ + 2ne^-$$

$$i_{total} = i_{film} + i_{dissolution} = \frac{\rho nF\upsilon}{M_w}\frac{d\theta}{dt} + i_o A e^{\frac{\eta}{\beta}}(1-\theta)$$

Current response is voltage and alloy dependent

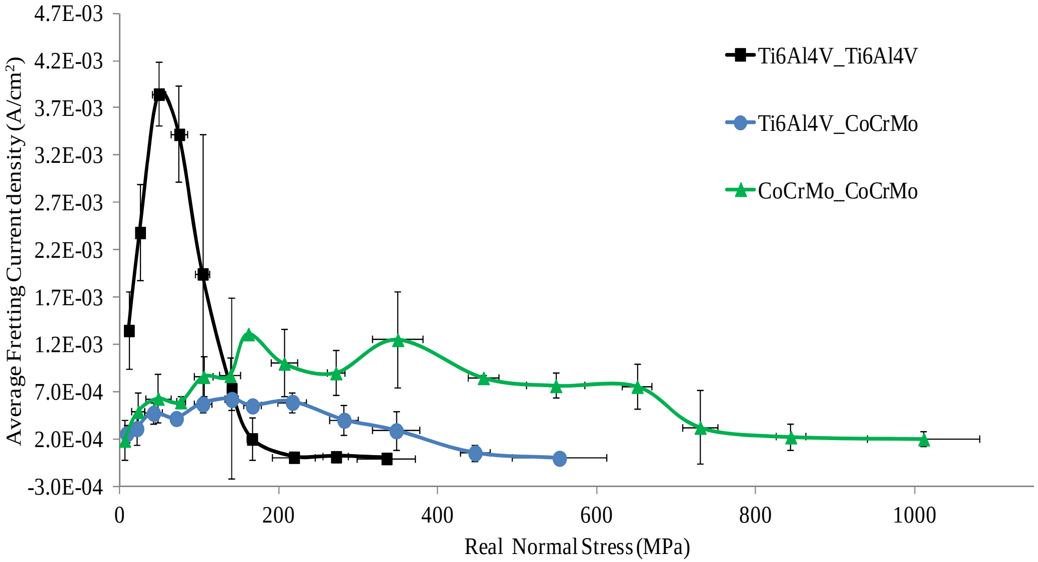
Buckley and Gilbert, 1994
Goldberg and Gilbert, 1997, 2004
Gilbert and Jacobs, ASTM, 1997

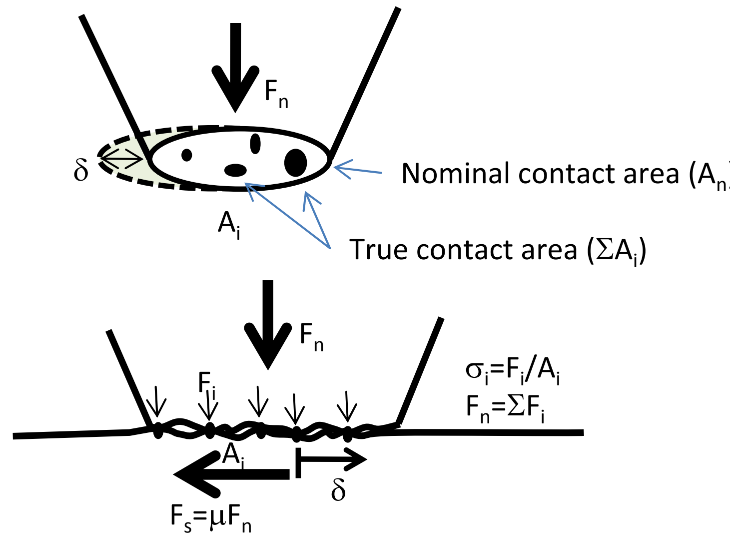
Asperity-Based Model of Fretting Corrosion Currents

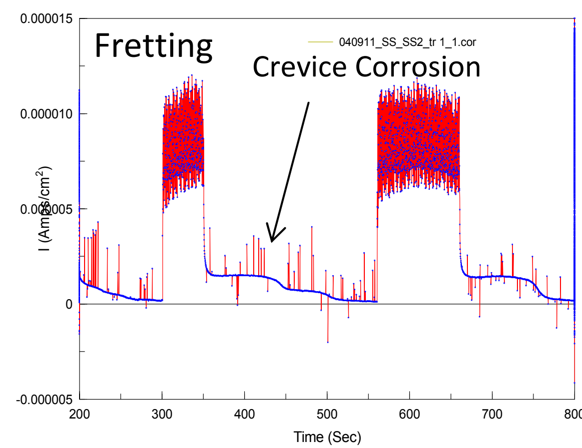
Swaminathan and Gilbert, 2012, Biomaterials

$$I_{film} = 2\frac{\rho n F}{M_w}\frac{A_{nom}}{\Delta} m(E - E^{onset})\frac{d\delta}{dt}$$

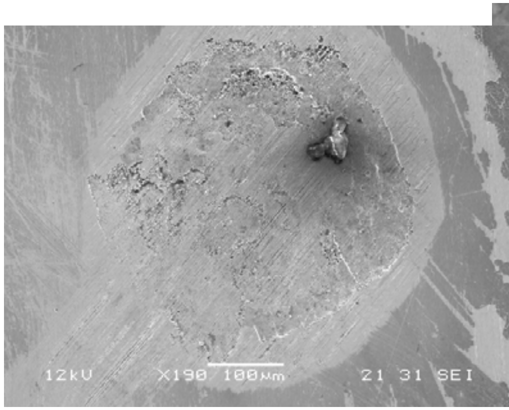
Fretting currents resulting from oxide abrasion and repassivation

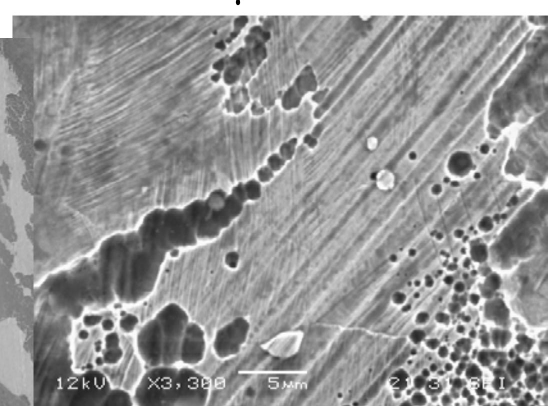






Note: Fretting 1 mm² will result in over 10 μA of current



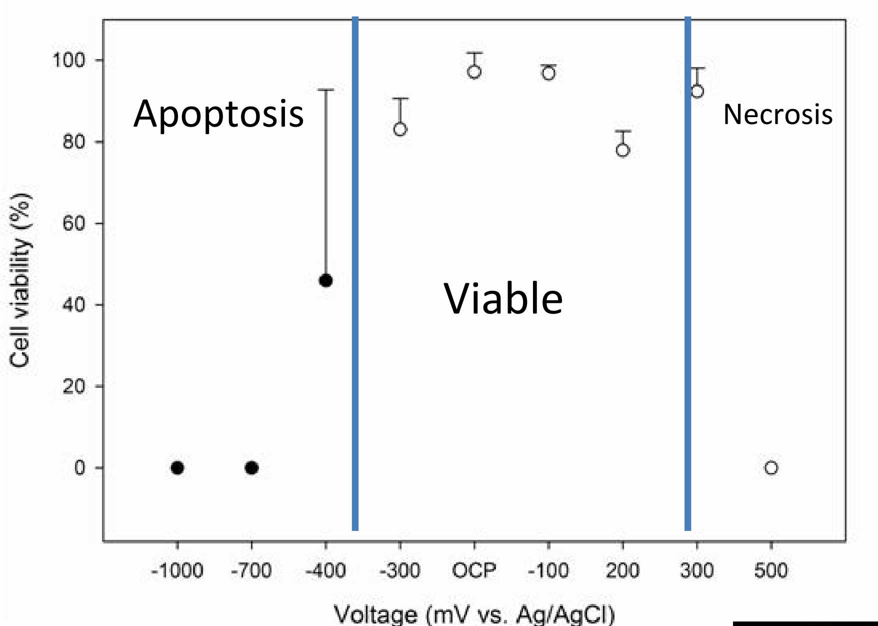


Fretting Initiated Crevice Corrosion

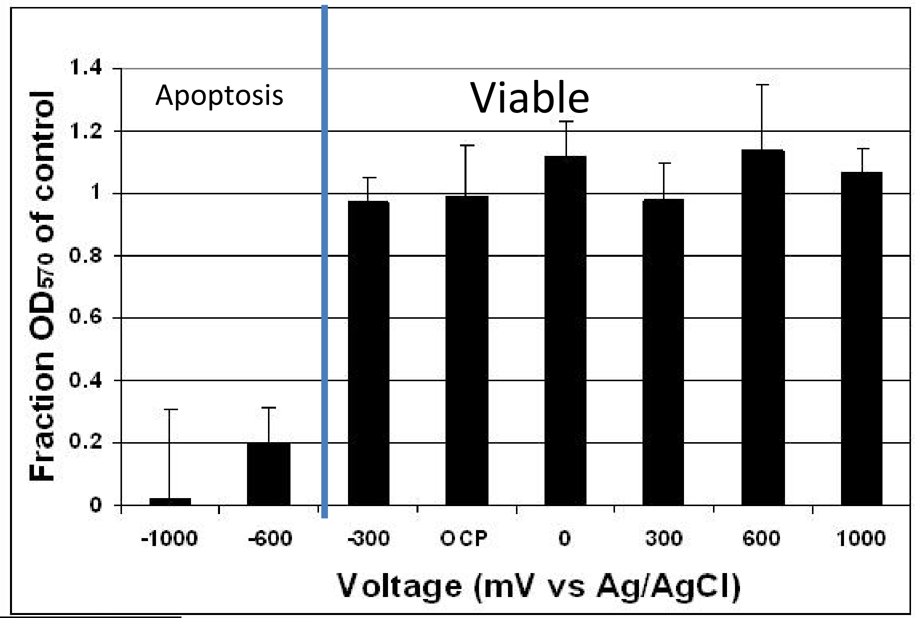
Reduction Reactions and Cell Viability (MC3T3-E1)

1 uA/cm^2 of reduction reaction kills cells

CoCrMo 24 hr at voltage, Haeri et al., 2012, Biomaterials



Cp-Ti, 24 hr at voltage, Erhensberger et al., JBMR-A, 2010

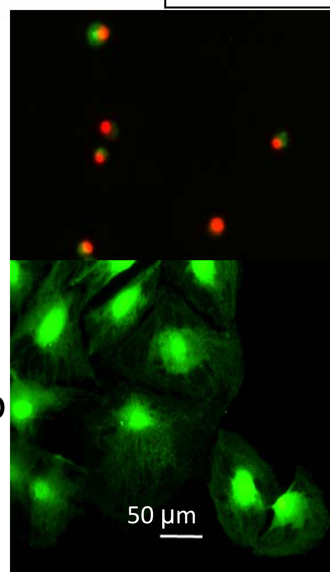


Reduction reactions at metal surfaces
Kill osteoblast-like cells

Previously unknown mechanism of biological interaction

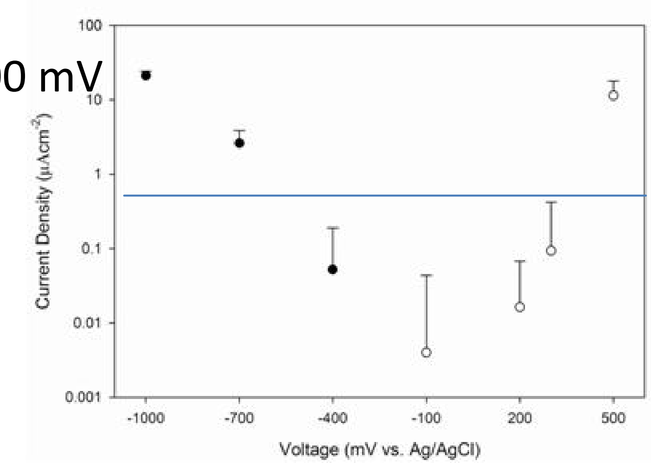
May play a role in hip prostheses in-vivo

It's not just about the metal ions



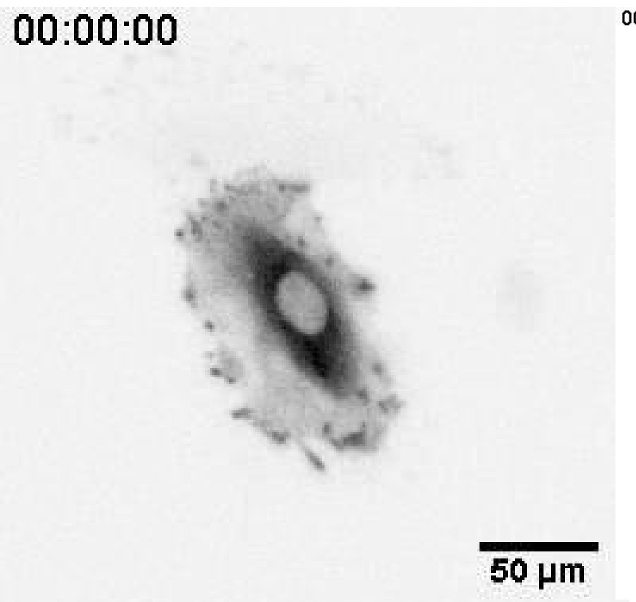
-1000 mV

OCP



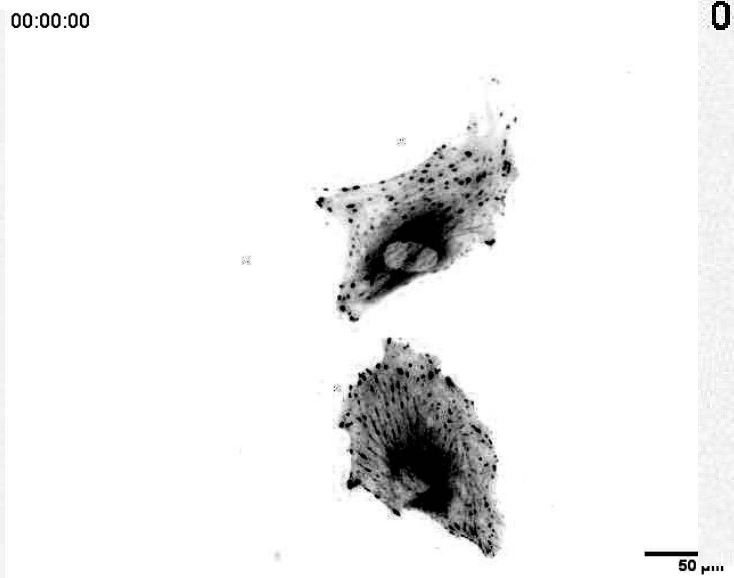
Animations of Cell Behavior Under Voltage Control

-400 mV



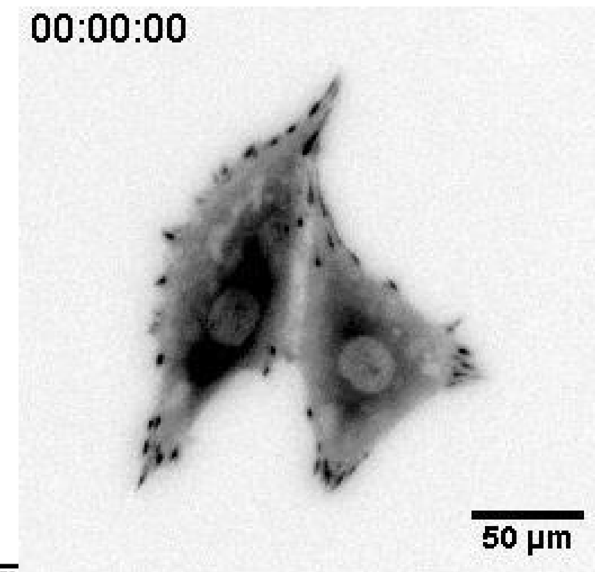
Apoptosis

Open Circuit Potential



Viable

+500 mV



Necrosis

Vinculin Fluorescence Thresholded and Fourier Transform Filtered.
(real time in upper left of each image)

Corrosion – Ion Level Estimate:
Can one estimate ion levels from corrosion currents?

Assume Steady State: Rate of generation of ions=rate of excretion via Urine

$$I = \sum_i \frac{n_i F}{Mw_i} \frac{dm_i}{dt}$$

$$I = \frac{dm}{dt} F \sum_i \frac{n_i \widehat{m}_i}{Mw_i}$$

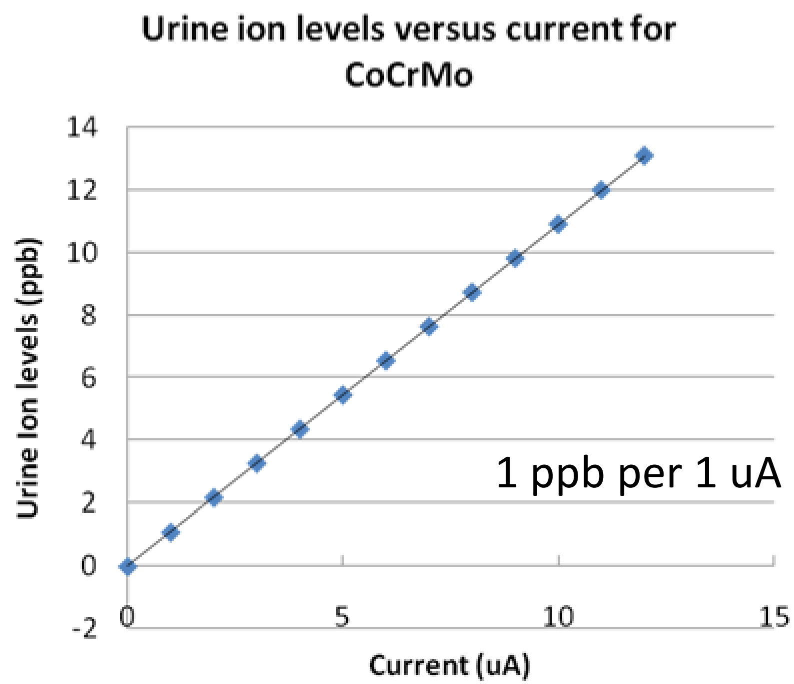
$$\dot{m} = kI$$

$$k = \frac{1}{F \sum_i \frac{n_i \widehat{m} i}{Mw_i}} = 2.18 \frac{\mu gs}{\mu Cday}$$

$$\rho_m = \frac{kI}{V_u}$$

$$Co \rightarrow Co^{2+} + 2e^-$$

$$Cr \rightarrow Cr^{3+} + 3e^-$$



ρ_m is metal ion levels in urine, I is the corrosion current, V_u is the volume of urine excreted per day (2 L)

This estimate (and its only an estimate) gives a sense of the relationship between amount of corrosion required to result in a systemic ion level

Conclusions

- Mechanically assisted corrosion (MAC) continues to be a serious concern for metallic biomaterials in all applications
- Wear and Corrosion are coupled and interactive
- Fretting can INITIATE crevice corrosion
- All current alloy systems are susceptible to MAC
- Negative voltage excursions result from MAC and may lead to adverse biological responses (apoptosis in-vitro)

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  - Medtronic, Stryker, Depuy
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